MAGNETIC STUDIES ON α—SILICON CARBIDE (α—SiC) CRYSTALS

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ABSTRACT. The magnetic susceptibility and anisotropy of different types of α-SiC, the wellknown high temperature semiconductor, have been measured at room temperature. The types of the samples were identified by X-rays and observation of colours and the results of measurements have been explained in the light of their crystal structures. It has been found that some of the samples are diamagnetic and others are freebly ferromagnetic. The field variation of the ferromagnetic samples have been studied both below and above saturation point and magnetic susceptibility of the paramagnetic part has been determined therefrom. The temperature variation of magnetic susceptibility and anisotropy of two varieties of diamagnetic samples have been measured from 90°K to 1000°K. Though the susceptibility increases considerably with temperature the anisotropy remains almost the same. The temperature variation of susceptibility upto a certain temperature obeys the relation $\chi \cdot D(kT)^{\alpha} e^{-\frac{\Delta E}{2kT}}$ with $\alpha = -\frac{1}{2}$.

INTRODUCTION

Silicon Carbide, the well-known high temperature semiconductor is obtained in several polymorphous modifications, one of which is cubic and is called β-SiC while the others are hexagonal or rhombohedral and are termed as α-SiC. The different modifications are obtained by the different stacking sequences of closest packed plane layers formed by silicon and carbon atoms for the three possible stacking positions, the different types being classified according to the number of layers needed to complete the stacking sequences (Azároff 1960).

These crystals which are mostly obtained commercially show different body colours arising probably from the presence of different foreign impurities like iron, aluminium, boron, magnesium, phosphorous, sulphur, fluorine, copper, nickel, zinc, antimony, nitrogen, vanadium, titanium etc (Knippenberg, 1963, Mellor). The best commercial grades are either pale green or pale yellow while the less purer grades are black or deep blue. Pure silicon carbide which is more difficult to prepare is transparent and almost colourless.

The electrical conductivity, Hall effect, Optical (1959) and other allied properties (Busch, 1946, Busch *et al.* 1946) of silicon carbide have been extensively studied over wide range of temperature (80°K to 1400°K). Results of these measurements have been utilised to ascertain its different electronic parameters.

But its magnetic properties which, it is wellknown, can furnish useful information regarding the electronic behaviours of such substances and the measurement of which are free from some major experimental difficulties encountered in electrical measurement (mainly contact difficulties) have not yet been seriously investigated. One finds only a preliminary report on some measurements on magnetic properties by Sigamony (1944) at room temperature alone, complete only for a green variety of the crystals, which obviously are inadequate for a theoretical analysis. We have therefore studied the magnetic properties of different varieties of α-silicon carbide crystals over wide range of temperatures and the present communication gives a preliminary account of such measurements with some crystals of α-SiC.

EXPERIMENTAL

The samples

Commercial variety of silicon carbide crystals were obtained in the form of blocks from Switzerland through the kindness of Prof. G. Busch of E.T.H., Zurich. These were cut into square or rectangular plates with diamond wheels avoiding contamination during cutting. Prior to any magnetic measurements the samples were tested for their structures by X-rays.

Magnetic Measurements :

The magnetic measurements consist of two parts, measurement of anisotropy and that of susceptibility.

Anisotropy

Magnetic anisotropy was measured by the method of critical torque well standardized here (Krishnan and Banerjee, 1936). For measurements at high temperatures the specimen is suspended in the tubular electric heater having non-inductive windings of nichrome wire, the pole pieces of the field magnet being protected from the heat by providing a water jacket round the heater. Interior of the experimental chamber was alwyas evacuated to maintain the same conditions as for susceptibility measurements. The temperatures were measured with a calibrated Pt—PtRh thermocouple. Since silicon carbide normally has a weak diamagnetism, which is expected to be temperature sensitive at higher temperatures only, measurements below room temperatures were taken at some fixed points only, namely, at the boiling points of liquid nitrogen (or oxygen) and melting point of carbondioxide.

Measurement of susceptibility

The magnetic susceptibility was measured with a Jewell-pivoted micro-balance described earlier (Das, 1963). Only modification that has been made in the previous arrangements is that the optical lever method of observing the deflection of

the balance has been replaced by a photo-cell method, which has considerably increased the deflectional sensitivity of the instrument. For both high and low temperature work the balance case along with the experimental chamber was always evacuated. This evacuation was particularly necessary at high temperatures to prevent the disturbances due to convection currents. Evacuation at low temperatures was done only to maintain the uniformity of experimental conditions. The method of production of high and low temperatures and their measurements were the same as already described in the case of anisotropy measurements. The crystals were attached to the suspension system with zinc oxyphosphate cement which stands very high temperatures and at the same time feebly diamagnetic. The crystals are always suspended with the (0001) plane vertical. The procedure for measurement was the same as described in an earlier paper (Das, 1963).

RESULTS

When crystals of SiC, usually diamagnetic, are suspended with (0001) planes vertical in a uniform magnetic field, in most cases they set with (0001) plane perpendicular to the field indicating that gm. molecular susceptibility $\chi_{\parallel}$ along the c-axis is algebraically greater than $\chi_{\perp}$ that along directions in the (0001) plane. Therefore the principal gm-molecular magnetic anisotropy of the crystal is $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$. The experimental values of $\Delta\chi$ and $\chi_{\parallel}$ for different specimens indexed A, B, C, D, E, F, G, H and I are shown in Table I. Any deviations from observations as stated above are also indicated there. The values of field independent average susceptibility and anisotropy as found by Sigamony (1944 are given in the same table for comparison. It is observed from the table that the anisotropies are not very high and hence the correction for the effect has to be considered. When the magnetic field is perfectly homogeneous, effect of shape is negligible (Nye 1957). But due to inhomogeneity of the field, an extra couple may act on the specimen while determining the anisotropies as well as the susceptibilities. In anisotropy measurements homogeneous magnetic field was used and thus the shape effect was negligible. In case of susceptibility measurements magnetic field was intentionally made inhomogeneous but the gradient was along the vertical direction while field was horizontal. Further the shape of the crystal was such that the principal shape direction and the principal susceptibility directions were coincident. So there will be no shape effect on the values of susceptibility determined.

In contrast to other samples, the samples *D* and *G* show field dependent paramagnetism, specimens always setting with their planes along the field. Measured anisotropies showed a marked difference in values for different directions of rotation of the torsion head and also showed field dependence obviously due to ferromagnetism. These have not been included in Table I. The part of the principal

TABLE I

Sample	Colour of the sample	Crystal class of the sample	Orientation of the c-axis w.r. to the field	$\Delta\chi \times 10^6$ per gm.mol	$\chi_{\parallel} \times 10^6$ per gm.mol	Anisotropy per.cent.
A	Pale green transparent.	Hexagonal 6H $a = 3.073$ Å $c = 15.08$ Å	C-axis $\parallel$ to field	0.91621	−10.618	8.1%
F	Light green transparent.	Hexagonal 6H $a = 3.073$ Å $c = 15.08$ Å	C-axis $\parallel$ to field	0.93111	−12.550	7.6%
I	Deep blue transparent.	Hexagonal 6H $a = 3.073$ Å $c = 15.08$ Å	C-axis $\parallel$ to field	0.87140	−10.376	7.9%
C	Black Opaque	Hexagonal 6H $a = 3.073$ Å $c = 15.08$ Å	C-axis $\parallel$ to field	0.90312	− 7.331	11.3%
H	Deep green transparent.	Hexagonal 6H mixed with Rhombohedral 15R.	C-a xis $\parallel$ to field	0.7780	− 7.321	9.9%
E	Light green transparent.	Rhombohedral 21R $a = 3.073$ Å $c = 52.78$ Å	C-axis $\parallel$ to field	0.93031	− 5.739	14.6%
B	Black Opaque	Rhombohedral mixture of 15R and 21R.	C-axis $\parallel$ to field	0.82279	− 4.200	17.3%
D	Yellowish green transparent.	Rhombohedral 15R $a = 3.073$ Å $c = 37.70$ Å	C-axis $\perp$ to field	—	$\chi_{\perp}$ = 123.744	—
G	Deep blue transparent.	Hexagonal 6H $a = 3.073$ Å $c = 15.08$ Å	C-axis $\perp$ to field	—	$\chi_{\perp}$ = 20.035	—
Sigamony's green sample		—	—	Average value of $\Delta\chi$ per gm. mol. = 0.82×10^{-6}	$\chi_{\perp}$ per gm. mol. = -13.1×10^{-6}	6.4%

susceptibility which is independent of the field, have however, been calculated from the slope of the linear portion of saturation region of the intensity-field curve.

These values represent the susceptibilities for direction in the (0001) plane and may therefore be called $\chi_{\perp}$. Temperature variation of $\Delta\chi$ and $\chi_{\parallel}$ of samples

A and B have been studied, as two typical cases from 90°K to about 1000°K and are shown graphically in figures 1 and 2. Study of temperature variation of other samples is also in progress and will be published in a future communication.

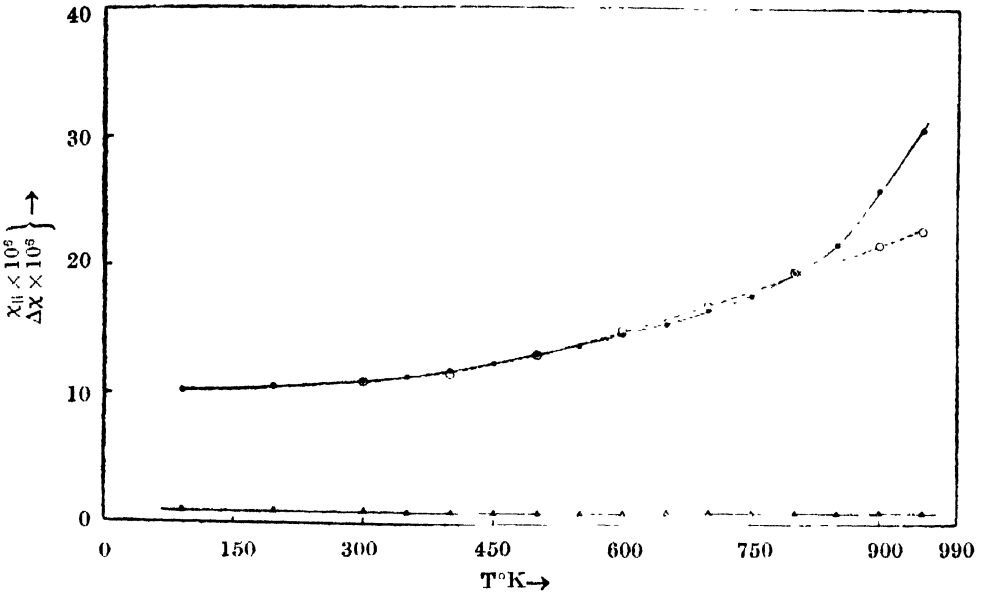

Fig. 1. Temperature variation of susceptibility ($\chi_{\parallel}$) and anisotropy ($\Delta\chi$) of sample—A
● Experimental values of $\chi_{\parallel} \times 10^6$
O Theoretically calculated values of $\chi_{\parallel} \times 10^6$
Δ Anisotropy $(\chi_{\parallel} - \chi_{\perp}) \times 10^6$

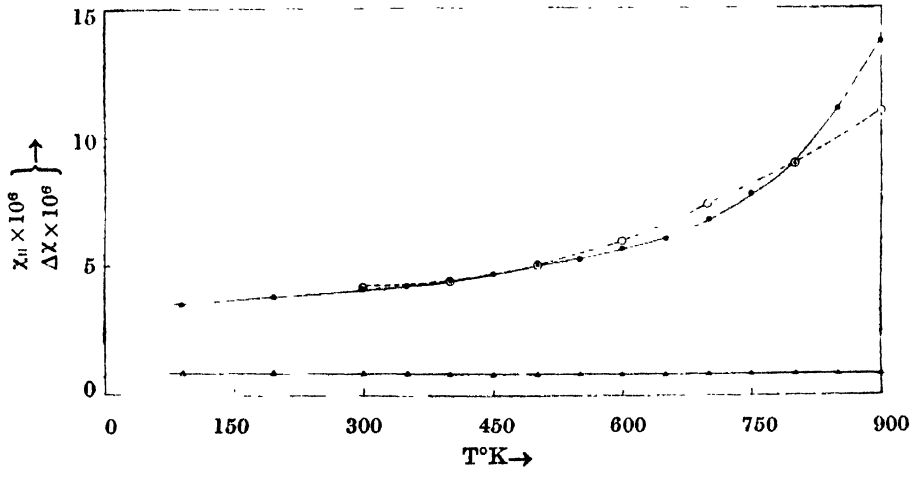

Fig. 2. Temperature variation of susceptibility ($\chi_{\parallel}$) and anisotropy ($\Delta\chi$) of sample—B.
● Experimental values of $\chi_{\parallel} \times 10^6$
O Theoretically calculated values of $\chi_{\parallel} \times 10^6$
Δ Anisotropy $(\chi_{\parallel} - \chi_{\perp}) \times 10^6$

DISCUSSION

As already stated, the present samples of SiC being of commercial variety contain different impurities and hence show various body colours (table I). In addition these may also have crystalline irregularities in them. So when discussing the properties of SiC crysals due consideration should be given to these facts.

It is evident from Table I that the values of $\Delta\chi$, the gram-molecular magnetic anisotropy of the different samples of α-Sic studied by us are small as compared to the values of graphite, molybdenite etc. ($\sim 1\times10^{6}$ C.G.S. e.m.u.) though the percentage anisotropy is pretty large ($\sim 17\%$ in some cases). These low values of $\Delta\chi$ can easily be accounted for from a consideration of the structures of different types of SiC. It is well known that the different polytypes of SiC crystal originate due to different stacking sequences of the hexagonal silicon and carbon layers (Jagodzinski *et al.* 1959). These stackings again seem to follow only such sequences that keep each silicon atom surrounded tetrahedrally by four carbon atoms and vice versa (Taylor *et al.* 1959). So the different polytypes of SiC, cubic, hexagonal or rhombohedral may be considered to be originating from the differences in the arrangements of these tetrahedra (Taylor *et al* 1959). In hexagonal and rhombohedral forms the deviations of arrangements of the tetrahedra from the cubic variety is found to be very small, the interatomic distances being nearly the same as in the cubic variety (Choyke and Patrick, 1959). To trace the origin of anisotropy one is quite justified to think that the stacking sequence will cause a distortion in the tetrahedra (which for convenience is being considered as repeating unit) which will effect both $\chi_{\parallel}$ and $\chi_{\perp}$ and hence $\Delta\chi$. One would therefore expect the anisotropy to be small in magnetic and other properties of α-SiC crystals (hexagonal or rhombohedral). It is further evident from Table I that almost all the samples (excepting samples* D and G) are diamagnetic—the susceptibility $\chi_{\parallel}$ for different samples varying from -4.2×10^{-6} C.G.S. e.m.u. per gm. mol. to -12.6×10^{-6} C.G.S. e.m.u. per gm. mol. This variation has therefore to be attributed to the differences in the nature and amounts of impurity contents of the different samples as also to crystalline defects, in addition to the distortion in the tetrahedra mentioned above. It may be pointed out here that magnetic anisotropy of the above mentioned aamples (except D and G) will remain unaffected by such foreign impurities and one should expect the same value of $\Delta\chi$ for all the samples but for differences in the distortion of the tetrahedra . Table I shows that the values of $\Delta\chi$ of all the samples are of the order 0.9×10^{-6} C.G.S. e.m.u. per gm. mol. excepting for samples B and H where admixture of different structures are found present. The percentage anisotropy shows larger variation. But it should be remembered that in percentage anisotropy the mean susceptibility is also a factor which, unlike anisotropy depends on many other

* These show field dependent paramagnetism due evidently to the nature of the impurity contents, and are excluded from present discussion.

factors as also on the distortion of the tetrahedra as stated before. This might cause the large variation in percentage anisotropy. Even then the least value of the percentage anisotropy in the table is not very small showing that the amounts of distortion produced in the tetrahedra are quite appreciable.

From figures 1 and 2 we find that $\Delta\chi$'s for samples A and B are practically independent of temperature and the values of $\chi_{\parallel}$'s for both the samples increase with temperature, the rate of increment being higher at higher temperatures. This indicates that $\chi_{\perp}$ will also increase with temperature nearly at the same rate as $\chi_{\parallel}$. This temperature dependent diamagnetism has obviously to be ascribed to the diamagnetism of thermally produced free charge carriers. But to account for the observed values of the susceptibilities, one should keep in mind the suggestion put forward at the beginning of this section, namely, the crystal contains both foreign impurities and crystalline defects. The observed susceptibilities may therefore be considered to be the combination of contributions of temperature independent diamagnetism from the crystal as well as from foreign impurities and defects, charge carrier susceptibilities due to intrinsic excitation as well as due to impurity levels and paramagnetic contribution of the impurities.

Therefore the observed susceptibility $\chi_{obs} = \chi_0 + \chi_c + \chi_{c'} + \chi_p$ where χ_c and $\chi_{c'}$ are the charge carrier susceptibilities χ_0, the temperature independent diamagnetic susceptibility and χ_p, the paramagnetic susceptibility. The values of χ_0 and χ_p are estimated in a manner suggested by Busch *et al.* (1960). For the charge carrier susceptibilities Busch *et al.* (1963) proposed an exponential variation with temperature. We accordingly tried to explain the temperature variation of the part of the susceptibility due to charge carrier, and obtained a relation of the type $\chi = D(kT)^{\alpha} e^{-\frac{\Delta E}{2kT}}$ where D and α are constants and ΔE is the activation energy. The observed values of the susceptibilities can be explained with the following values of D, α and ΔE.

TABLE II

Sample	D	α	ΔE in e.volts	ΔE from electrical conductivity in e.volts (Busch, 1946)
A	2.6868	− 1/4	0.3196	0.304
B	2.8503	− 1/4	0.4557	0.270

The values of ΔE may be compared with those obtained by Busch (1946) from electrical conductivity measurements with samples having almost similar body colour and structures. It should however be noted in this connection that though the agreement between the observed and calculated values are fair at low temperatures, at higher temperatures the differences between the two sets of values

are quite appreciable (fig. 1. and 2). It may be due to the fact that the extrinsic and intrinsic contribution could not be separately estimated. In order, therefore, to explain the observed magnetic properties of these two samples as well as other samples extensive studies of the magnetic and allied properties of SiC have been undertaken and work is in progress.

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